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PATENT SPECIFICATION

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(54) FUNGICIDALLY ACTIVE 1,3,4-THIADIAZOLE DERIVATIVES

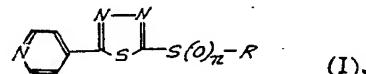
(71) We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with fungicidally active 1,3,4-thiadiazole derivatives for controlling phytopathogenic fungi, and with their use.

Fungicidally active substances based on 1,2,4-thiadiazole have been known (cf. United States Specifications Nos. 3,260,588 and 3,260,725). 5-Ethoxy-3-trichloromethyl-1,2,4-thiadiazole, however, which is distinguished by its special fungicidal property has only a specific activity against *Pythium*.

It has also been proposed to use 2-halogenoalkyl-5-alkylsulphinyl-1,3,4-thiadiazoles and the corresponding sulphonyl compounds against phytopathogenic fungus pests (cf. German Offenlegungsschrift No. 1,817,069). These active substances do not, however, have a sufficient compatibility with plants.

The present invention provides compounds of the general formula I



in which R represents an aliphatic hydrocarbon group which preferably contains 1 to 5 carbon atoms and n represents 1 or 2, and salts of such compounds. It is to be understood in the description and claims herein that the salts of the compounds of the general formula I include not only salts with inorganic and organic acids but also salts with Lewis acids.

The compounds of the general formula I and their salts not only have an activity against phytopathogenic fungus pests but also have a good compatibility with plants.

The present invention accordingly also provides a fungicidal preparation which comprises a compound selected from compounds of the general formula I and salts of such compounds, in admixture or conjunction with a suitable carrier. The preparations may of course contain one or more of the active substances.

The present invention further provides a method of protecting a living plant against phytopathogenic fungi, wherein a living plant is treated with a compound selected from compounds of the general formula I and their salts.

The present invention further provides a method of treating a crop area against phytopathogenic fungi, wherein a crop area is treated with a compound selected from compounds of the general formula I and their salts.

The present invention further provides a method of protecting seeds against phytopathogenic fungi, wherein seeds are treated with a compound selected from compounds of the general formula I and their salts.

Particularly suitable active compounds of the above general formula I are compounds in which R represents a linear or branched alkyl group containing 1 to 5 carbon atoms, for example a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl or pentyl group.

[Price 33p]

These active compounds may be applied either in their free form or in the form of their salts with inorganic or organic acids.

As salt-forming acids there may be mentioned, for example, inorganic acids, for example mineral acids, for example hydrochloric or sulphuric acid, and organic acids, for example oxalic or para-toluenesulphonic acid.

Furthermore, there may be mentioned the so-called Lewis acids, for example boron trifluoride or zinc chloride, which form reaction products with the compounds of the general formula I.

The compounds of the general formula I and their salts used in accordance with the present invention are distinguished by a broad activity spectrum against pathogens carried by seeds or in the soil and this activity is substantially greater than that of the aforesaid known preparations based on halogenoalkyl-thiadiazole derivatives and that of methyl-1-(butylcarbamoyl)-2-benzimidazole-carbamate, 1,4-dichloro-2,5-dimethoxybenzene, 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole and *p*-(dimethylamino)-benzenediazo-sodium sulphonate.

These compounds are active, for example, against *Pythium*, *Rhizoctonia*, *Tilletia*, *Helminthosporium* and other phytopathogenic fungus pests and are suitable for their complete control. In addition, the active substances display an outstanding compatibility with plants which is substantially better than that of the aforesaid known halogenoalkyl-thiadiazole derivatives.

Particularly suitable as fungicides are, for example, 2-(4-pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole dihydrogensulphate and 2-(4-pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrochloride for combating cereal diseases, and 2-(4-pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogen sulphate monohydrate for combating soil-specific pathogens on cotton and sugar beets, combined with a minimum effect on the plants.

The compounds of the general formula I and their salts may therefore be used in agriculture and horticulture for general soil treatment, for treating seed materials or for treating seed furrows. Such a treatment combats not only fungus pests that attack from the soil but also those which are carried by seeds and are parasites found on the parts above the ground. Surprisingly, some of the fungicides used according to the present invention display systemic properties.

In each application the active substances may be used either individually or as mixtures containing at least two of the active substances or, if desired, in admixture with other plant protective agents and pest control agents, for example with insecticides, when it is desired to control these or other pests at the same time. It is also possible to admix them with synergistically active compounds.

The fungicidal preparations advantageously take the form of, for example, powders, spraying or dusting agents, granules, solutions, emulsions or suspensions, with the addition of solid and/or liquid diluents or vehicles and, if desired, of surface active agents, for example adhesives, wetting agents, emulsifiers and/or dispersing agents.

Suitable liquid vehicles are, for example, water, mineral oils and other organic solvents, for example xylene, chlorobenzene, chloroform, 1,3-dichloropropene, cyclohexanone, ether, ethyl acetate, dimethylformamide and dimethylsulphoxide.

Suitable solid vehicles are, for example, lime, attaclay and other clays, kaolin, chalk and talcum as well as natural or synthetic silicic acid.

As surface-active agents there may be mentioned, for example, salts of ligninsulphonic acids, salts of alkylated benzenesulphonic acids, sulphonated acid amides and their salts, polyethoxylated amines and alcohols.

If it is desired to use the active substances for seed dressings, it is also possible to admix colouring matter with them to impart a clearly visible coloration to the dressed seed material.

The total amount in the fungicidal preparations of the active compound(s) selected from compounds of the general formula I and their salts may be varied within wide limits; the actual concentration of the active substance used in the preparation depends mainly on the amount of preparation that is to be used, for example, for the treatment of soil or seed material. The preparations may contain, for example, from approximately 1 to 80%, preferably from approximately 10 to 50%, of active substance(s) and from approximately 99 to 20% of liquid or solid vehicles and, if desired, up to 20% of surface-active agent(s), all the percentages being by weight. The various forms of application are manufactured in a known manner, for example by grinding or mixing processes.

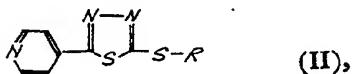
To promote the emergence of seedlings the preparations are applied in the usual manner before sowing either directly on to the seed material or put into the seed fur-

rows together with the seeds (the so-called combined seeding and drilling method). For a treatment of the soil as such it is advantageous to introduce the preparation into the topmost soil layers down to a depth of about 20 cm, for example by rotary hoeing.

5 The compounds of the general formula I may be manufactured by known methods, for example by the process described below which is also included within the scope of the present invention.

The present invention accordingly further provides a process for the manufacture of a compound of the general formula I or a salt thereof, wherein a compound of the general formula II

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in which R has the meaning given above, is treated with an oxidizing agent, and, if desired, the resulting free compound is converted into a salt thereof by reaction with an inorganic or organic acid or a Lewis acid.

15 The oxidizing agent used for the manufacture of a compound of the general formula I, in which $n = 1$, is preferably an organic hydroperoxide, for example tertiary butylhydroperoxide, or a per-acid, for example *m*-chloroperbenzoic acid, or an N-halogeno-acid amide, for example N-bromosuccinimide, or an inorganic compound, for example hydrogen peroxide or sodium metaperiodate. The quantity of the oxidizing agent used for this purpose is two oxidation equivalents or a small excess for every mole 20 of thio compound, at a temperature ranging from about 0° to 60°C.

To manufacture a compound of the general formula I in which $n = 2$ there may be used apart from the afore-mentioned oxidizing agents certain inorganic agents, for example potassium permanganate or chromic acid or a salt thereof or nitric acid at a 25 temperature of about 0° to 120°C. For this purpose there are used for 1 mole of the thio compound accordingly 4 oxidation equivalents or an excess thereof, that is to say at least twice as much as for the sulphoxidation described above, in which $n = 1$.

30 Suitable reaction media are organic solvents, for example carboxylic acids, for example acetic acid, ethers, for example dioxan, ketones, for example acetone, acid amides, for example dimethylformamide, nitriles, for example acetonitrile, or other solvents that are inert towards the above-mentioned oxidizing agents, either by themselves or in admixture with water.

The yields are good and amount to 60 to 95% of the theoretical yield.

35 The salts of the compounds of the general formula I are manufactured by the direct reaction of inorganic or organic acids upon compounds of the general formula I. As inorganic acids there may be mentioned, for example, mineral acids, for example hydrochloric and sulphuric acids, and as organic acids there may be mentioned, for example, oxalic and *p*-toluene sulphonic acids. As Lewis acids there may be mentioned zinc chloride and boron trifluoride. The solvents used are those that are inert towards the reactants, among which there may be mentioned, for example, aliphatic and aromatic 40 hydrocarbons and halogenated hydrocarbons, for example petroleum ether, benzene, methylene chloride, chlorinated ethylenes, ketones, ether-like compounds, N,N-dialkylated amides, nitriles and alcohols, that is to say all substances which themselves have neither acidic nor basic properties.

45 Examples 1 to 3 below illustrate the process of the present invention.

Some compounds used in accordance with the present invention are listed in the following Table; the number "II" is used after "zinc", "mercury", "copper", "calcium", "manganese", "nickel" and "cobalt" to denote that each of these metals is divalent in the compounds indicated.

Name of Compound	Melting Point, °C
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole	186
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole-dihydrogensulphate monohydrate	173 (with decomposition)
2-(4-Pyridyl)-5-methylsulphiny1-1,3,4-thiadiazole	149
2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole hydrochloride	211
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole hydrochloride	171 (with decomposition)
2-(4-Pyridinyl)-5-isopropylsulphonyl-1,3,4-thiadiazole	146
2-(4-Pyridinyl)-5-ethylsulphiny1-1,3,4-thiadiazole hydrobromide	173 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole hydrogennitrate	162 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole methyl-hydrogensulphate	139 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole dihydrogenoxalate	183 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole dihydrogenmaleate	125 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole hydrogen-methanesulphonate	173 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole hydrogen-4-toluenesulphonate	143 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole boron trifluoride adduct	160 (with decomposition)
Bis-[2-(4-pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole]-zinc-II-chloride adduct	260 (with decomposition)
Bis-[2-(4-pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole]-mercury-II-chloride adduct	186 (with decomposition)
Bis-[2-(4-pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole]-copper-II-chloride adduct	230 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole hydrogenperchlorate	173 (with decomposition)
Bis-[2-(4-pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole]-calcium-II-chloride adduct	above 340
Bis-[2-(4-Pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole]-manganese-II-chloride adduct	above 340
Bis-[2-(4-pyridyl)-5-ethylsulphiny1-1,3,4-thiadiazole]-nickel-II-chloride adduct	above 340

Name of Compound	Melting Point, °C
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenmethanesulphonate	222 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogenmaleate	155 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogenoxalate	203 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogennitrate	217 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenbromide	260 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenperchlorate	239 (with decomposition)
Bis-[2-(4-pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole]-cobalt-II-chloride adduct	above 340
Bis-[2-(4-pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole]-zinc-II-chloride adduct	296 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogeniodide	255 (with decomposition)
Bis-[2-(4-pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole]-cobalt-II-chloride adduct	296 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole-hydrogen-4-toluenesulphonate	210
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrochloride	250 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole trihydrogenphosphate	170 (with decomposition)
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole borontrifluoride adduct	265 (with decomposition)
Bis-[2-(4-pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole]-mercury-II-chloride adduct	228 (with decomposition)
2-(4-Pyridyl)-5-butylsulphonyl-1,3,4-thiadiazole dihydrogensulphate	159
2-(4-Pyridyl)-5-propylsulphanyl-1,3,4-thiadiazole	103
2-(4-Pyridyl)-5-butylsulphanyl-1,3,4-thiadiazole	77
2-(4-Pyridyl)-5-propylsulphanyl-1,3,4-thiadiazole dihydrogensulphate	157
2-(4-Pyridyl)-5-butylsulphanyl-1,3,4-thiadiazole dihydrogensulphate	138 (with decomposition)
2-(4-Pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole-hydrogen-trifluoromethane sulphonate	156 (with decomposition)

The compounds listed above and the products of Examples 1 to 3 are soluble in water and in organic solvents, for example xylene, cyclohexanone, methylene chloride, ethylene chloride, chloroform, dichloropropene, ether, ethyl acetate, dimethylformamide and dimethylsulphoxide.

5 The following Examples illustrate the invention. As stated above, Examples 1 to 3 describe the manufacture of active compounds of the present invention, and Examples 4 to 9 illustrate the fungicidal activity of some of the active substances used according to the present invention as compared with that of known fungicidally active substances.

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10 Example 1.
A solution of 22.3 g of 2-(4-pyridyl)-5-ethylthio-1,3,4-thiadiazole in 250 ml of glacial acetic acid prepared at about 35°C was mixed with 11.3 g of hydrogen peroxide of 30% strength, allowed to stand overnight and the solvent was then distilled off. The residue was recrystallized from ethanol. Yield: 23.5 g of 2-(4-pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole melting at 108°C.

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15 Example 2.
A solution of 11.3 g of 2-(4-pyridyl)-5-ethylthio-1,3,4-thiadiazole in 75 ml of glacial acetic acid and 25 ml of water was mixed at 40°C with 10.5 g of potassium permanganate. The reaction mixture was then stirred for 2 hours, then cooled to 10°C and an aqueous sodium bisulphite solution was added until the reaction solution was colourless. The precipitated 2-(4-pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole was filtered off and recrystallized from ethanol.
Yield: 10.6 g melting at 142°C.

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20 Example 3.
25 4.5 g of sulphuric acid of 95% strength were slowly stirred into a solution of 10 g of 2-(4-pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole in 100 ml of tetrahydrofuran. The mixture was stirred for 30 minutes, then cooled and the precipitate was filtered off with suction. The dried 2-(4-pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole dihydrogensulphate (13 g) melted at 168°C with decomposition.

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30 Example 4.
30 Steamed compost soil was inoculated with mycelium of *Pythium ultimum* or *Rhizoctonia solani*. In a series of experiments cotton seeds dressed with preparations of 50% strength were sown in the soil contained in earthenware dishes of 2 litre capacity in an amount of 50 seeds per dish. After allowing the seeds to grow for 14 days at 24° to 26°C the cotton seedlings that had remained sound were counted.

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Sound cotton seedlings (% of the seeds used)

Active compound in preparation of the present invention	0.5 g of active compound per kg of seeds	
	Pythium	Rhizoctonia
2-(4-pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole	34%	28%
2-(4-pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogensulphate monohydrate	54%	58%
2-(4-pyridyl)-5-methylsulphinyl-1,3,4-thiadiazole	16%	28%
2-(4-pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole	36%	18%
<u>Control compound in preparation</u>		
methyl-1-(butylcarbamoyl)-2-benzimidazole-carbamate	0%	56%
1,4-dichloro-2,5-dimethoxybenzene	0%	42%
5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole	16%	6%
p-(dimethylamino)-benzene-diazo sodium sulphonate	12%	4%
Infested soil, seeds undressed	0%	4%
Steamed soil, seeds undressed	82%	

Example 5.

Sugar beet seeds (monogermin) dressed with preparations of 50% strength were planted in a series of experiments in normal compost soil (containing fungi of the damping-off complex) in an amount of 100 seeds per concentration. After 14 days' growth at 22 to 24°C the experiment was evaluated.

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Sound sugar beet seedlings (% of seedlings used)

Active compound in preparation of the present invention	1 g of active compound per kg of seeds		2 g of active compound per kg of seeds
	79%	80%	
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogensulphate monohydrate			
<u>Control compound in preparation</u>			
tetramethylthiuram disulphide	35%	38%	
Infested soil, seeds undressed	20%		
Steamed soil, seeds undressed	77%		

Example 6.

Sugar beet seeds (monogerm) infested by *Phoma betae* were dressed with preparations of 50% strength and sown in a series of experiments in steamed compost soil in an amount of 100 seeds per concentration. After 3 weeks' growth at 22 to 24°C the experiment was evaluated.

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Active compound in preparation of the present invention	% of sound plants emerged after 3 weeks	
	1 g of active compound per kg of seeds	2 g of active compound per kg of seeds
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogensulphate monohydrate	58%	87%
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenmethanesulphonate	73%	79%
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogenoxalate	61%	83%
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogennitrate	77%	83%
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenbromide	74%	77%
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogeniodide	72%	78%
Bis-[2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole] zinc-II chloride adduct	84%	77%
Bis-[2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole] cobalt-II chloride adduct	69%	89%
Control compound in preparation		
Tetramethylthiuram disulphide	30%	66%
Infested, undressed seed material		21%

Example 7.

Barley seeds naturally infested by *Helminthosporium gramineum* were thoroughly mixed in a series of experiments with the compound under test, then sown in soil and kept in an air-conditioned chamber at 5 to 10°C. After 3—4 weeks the extent of infection as a percentage of the affected primary leaves was determined. To ensure an even distribution of the active compound all over the grains the compounds under test were admixed with the usual additives, for example kaolin, talcum, chalk, colouring matter and oil. For this series of experiments an average of 478 plants per compound under test was used. For comparison seed material was treated with methoxyethyl-mercury-silicate (6.9% in a commercial dry dressing).

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Active compound in preparation of the present invention	Relative infection as % with g of active compound/100 kg of barley	
	25 g	10 g
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole	5	12
2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogensulphate monohydrate	5	14
2-(4-Pyridyl)-5-methylsulphanyl-1,3,4-thiadiazole	1.4	6
2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole	0.6	0.4
2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole hydrochloride	0.3	0.7
2-(4-Pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole	0	0
2-(4-Pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole dihydrogensulphate	0	0.2
2-(4-Pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole hydrochloride	0.1	0.2
2-(4-Pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole hydrogenperchlorate	0.3	0.3
Bis-[2-(4-pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole] calcium-II chloride adduct	0.3	0
Bis-[2-(4-pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole] manganese-II chloride adduct	0.3	1.3
Bis-[2-(4-pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole] nickel-II chloride adduct	0	0.7
<u>Control compound in preparation</u>		
Methoxyethyl-mercury-silicate	0	0.7
Untreated	100 (48% absolute)	

Example 8.

In a further series of experiments with barley seed material infested by *Helminthosporium* the activity against the stripe disease on barley of the water-insoluble compound 2-(4-pyridyl)-5-ethylsulphanyl-1,3,4-thiadiazole and of its water-soluble hydrochloride and sulphate was tested. In this series of experiments an average of 421 plants per individual compound under test was used. The two water-soluble compounds in the requisite amounts were dissolved in 1 litre of water and thoroughly mixed with 100 kg of barley in each case. The control compound used was methoxyethyl-mercury-silicate.

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Active compound in preparation of the present invention	Form of application	Relative infection as % at...g of active compound/100 kg of barley	
		25 g	10 g
2-(4-Pyridyl)-5-ethylsulphinyl- 1,3,4-thiadiazole	Powder	0.5	0.7
2-(4-Pyridyl)-5-ethylsulphinyl- 1,3,4-thiadiazole dihydrogensulphate	Powder	0.2	0.2
2-(4-Pyridyl)-5-ethylsulphinyl- 1,3,4-thiadiazole hydrochloride	Powder	0.5	1.2
2-(4-Pyridyl)-5-ethylsulphinyl- 1,3,4-thiadiazole dihydrogensulphate	Liquid	0	0.5
2-(4-Pyridyl)-5-ethylsulphinyl- 1,3,4-thiadiazole hydrochloride	Liquid	0	1.2
<u>Control compound in preparation</u>			
Methoxyethyl-mercury-silicate	Powder	1	6.4
Untreated			100 (25% absolute)

Example 9.

5 In a further series of experiments the activity of the compounds listed in the following Table against the stripe disease on barley (*Helminthosporium gramineum*) and stinking smut of wheat (*Tilletia caries*) was compared in a field test. The seeds were thoroughly dressed with the amounts of active compounds, prepared as described in Example 7, shown in the Table, and the seeds were sown on each of 3 plots. The figures shown in the Table are degrees of absolute infection as a percentage of the total number of plants on the 3 plots. For this series of experiments the average number of plants per compound under test was 1027 in the case of winter barley and 1070 in the case of winter wheat. The control compounds used were methoxyethyl-mercury-silicate and known thiadiazole derivatives.

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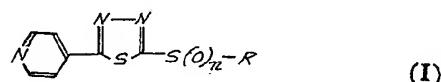
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Active compound in preparation of the present invention	Form of application	% infection at . . . g of active compound/100 kg of			
		Winter barley		Winter wheat	
		50	25	50	25
2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole	Powder	—	—	1.0	2.2
2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole hydrochloride	Powder	—	—	0.7	2.7
2-(4-Pyridyl)-5-ethylsulphinyll-1,3,4-thiadiazole	Powder	0.1	0.4	0.2	0.1
2-(4-Pyridyl)-5-ethylsulphinyll-1,3,4-thiadiazole dihydrogensulphate	Powder	0	0.1	4.1	6.3
2-(4-Pyridyl)-5-ethylsulphinyll-1,3,4-thiadiazole hydrochloride	Powder	—	—	1.3	1.5
2-(4-Pyridyl)-5-ethylsulphinyll-1,3,4-thiadiazole dihydrogensulphate	Liquid	0	0.3	0	0.1
2-(4-Pyridyl)-5-ethylsulphinyll-1,3,4-thiadiazole hydrochloride	Liquid	—	—	0	0.3
<u>Control compound in preparation</u>					
2-Trifluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	Powder	0.3	—	1.7	8.9
2-Dichloromethyl-5-methylsulphinyll-1,3,4-thiadiazole	Powder	1.8	2.7	—	—
2-Trifluoromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	Powder	—	—	8.7	19
Methoxymercury-silicate	Powder	0	—	0	—
Untreated			4.8		49

WHAT WE CLAIM IS:—

1. A compound of the general formula I

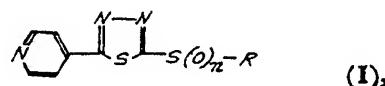


- 5 in which R represents an aliphatic hydrocarbon group and n represents 1 or 2.
 2. A compound as claimed in claim 1, wherein R represents an aliphatic hydrocarbon group containing up to 5 carbon atoms.
 3. A compound as claimed in claim 2, wherein R represents an alkyl group containing 1 to 5 carbon atoms.
 10 4. A salt of a compound as claimed in any one of claims 1 to 3.
 5. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogensulphate monohydrate.

6. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole dihydrogensulphate.
 7. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrochloride.
 8. 2-(4-Pyridyl)-5-isopropylsulphonyl-1,3,4-thiadiazole.
 9. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrobromide.
 10. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrogennitrate. 5
 11. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole methylhydrogensulphate.
 12. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole dihydrogenoxalate.
 13. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole dihydrogenmaleate.
 14. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrogenmethanesulphonate.
 15. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrogen-4-toluenesulphonate. 10
 16. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole borontrifluoride adduct.
 17. Bis-[2-(4-pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole]-zinc-II-chloride adduct.
 18. Bis - [2 - (4 - pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole] - mercury-II - chloride adduct. 15
 19. Bis - [2 - (4 - pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole] - copper-II - chloride adduct. 15
 20. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole.
 21. 2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole.
 22. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole. 20
 23. 2-(4-Pyridyl)-5-methylsulphinyl-1,3,4-thiadiazole.
 24. 2-(4-Pyridyl)-5-ethylsulphonyl-1,3,4-thiadiazole hydrochloride.
 25. 2-(4-Pyridyl)-5-ethylsulphinyl-1,3,4-thiadiazole hydrogenperchlorate.
 26. Bis - [2 - (4 - pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole] - calcium-II - chloride adduct. 25
 27. Bis - [2 - (4 - pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole] - manganese-II - chloride adduct. 25
 28. Bis - [2 - (4 - pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole] - nickel-II - chloride adduct. 25
 29. 2 - (4 - Pyridyl) - 5 - methylsulphonyl - 1,3,4 - thiadiazole hydrogen-methanesulphonate. 30
 30. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogenmaleate.
 31. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole dihydrogenoxalate.
 32. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogennitrate.
 33. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenbromide.
 34. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole hydrogenperchlorate. 35
 35. Bis - [2 - (4 - pyridyl) - 5 - methylsulphonyl - 1,3,4 - thiadiazole] - cobalt-II - chloride adduct.
 36. Bis - [2 - (4 - pyridyl) - 5 - methylsulphonyl - 1,3,4 - thiadiazole] - zinc-II - chloride adduct. 40
 37. 2 - (4 - Pyridyl) - 5 - methylsulphonyl - 1,3,4 - thiadiazole hydrogeniodide.
 38. Bis - [2 - (4 - pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole] - cobalt-II - chloride adduct. 40
 39. 2 - (4 - Pyridyl) - 5 - methylsulphonyl - 1,3,4 - thiadiazole hydrogen - 4 - toluenesulphonate.
 40. 2-(4-Pyridyl)-5-methylphonyl-1,3,4-thiadiazole hydrochloride. 45
 41. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole trihydrogenphosphate.
 42. 2-(4-Pyridyl)-5-methylsulphonyl-1,3,4-thiadiazole borontrifluoride adduct.
 43. Bis - (2 - (4 - pyridyl) - 5 - methylsulphonyl - 1,3,4 - thiadiazole) - mercury-II - chloride adduct. 50
 44. 2-(4-Pyridyl)-5-butylsulphonyl-1,3,4-thiadiazole dihydrogensulphate.
 45. 2-(4-Pyridyl)-5-propylsulphinyl-1,3,4-thiadiazole. 50
 46. 2-(4-Pyridyl)-5-butylsulphinyl-1,3,4-thiadiazole.
 47. 2-(4-Pyridyl)-5-propylsulphonyl-1,3,4-thiadiazole dihydrogensulphate.
 48. 2-(4-Pyridyl)-5-butylsulphonyl-1,3,4-thiadiazole dihydrogensulphate. 55
 49. 2 - (4 - Pyridyl) - 5 - ethylsulphinyl - 1,3,4 - thiadiazole - hydrogentrifluoromethanesulphonate.
 50. A fungicidal preparation which comprises a compound selected from compounds of the general formula I given in claim 1, in which R and n have the meanings given in claim 1, and salts of such compounds of the general formula I, in admixture or conjunction with a suitable carrier. 60
 51. A fungicidal preparation which comprises the compound claimed in any one of claims 5 to 24, in admixture or conjunction with a suitable carrier.
 52. A fungicidal preparation which comprises the compound claimed in any one of claims 25 to 49, in admixture or conjunction with a suitable carrier.

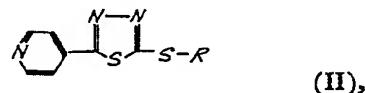
53. A preparation as claimed in any one of claims 50 to 52, which is in the form of a powder, a spraying or dusting agent, granules, a solution, an emulsion or a suspension. 5
54. A preparation as claimed in any one of claims 50 to 53, containing a single compound selected from compounds of the general formula I and salts thereof in an amount of approximately 1 to 80% by weight. 5
55. A preparation as claimed in any one of claims 50 to 53, containing two or more compounds selected from compounds of the general formula I and salts thereof in a total amount of approximately 1 to 80% by weight. 10
56. A preparation as claimed in claim 54 or 55, wherein the amount or the total amount, respectively, is approximately 10 to 50% by weight. 10
57. A preparation as claimed in any one of claims 50 to 56, containing a single surface-active agent in an amount of up to 20% by weight. 15
58. A preparation as claimed in any one of claims 50 to 56, containing two or more surface-active agents in a total amount of up to 20% by weight. 15
59. Any one of the fungicidal preparations as claimed in claim 50 and substantially as described in Examples 4, 5, 8 and 9 herein. 15
60. Any one of the fungicidal preparations as claimed in claim 50 and substantially as described in Examples 6 and 7 herein. 20
61. A method of protecting a living plant against phytopathogenic fungi, wherein a living plant is treated with a compound selected from compounds of the general formula I given in claim 1, in which R and n have the meanings given in claim 1, and salts of such compounds of the general formula I. 20
62. A method as claimed in claim 61, wherein the living plant is treated with the compound claimed in any one of claims 5 to 24. 25
63. A method as claimed in claim 61, wherein the living plant is treated with the compound claimed in any one of claims 25 to 49. 25
64. A method as claimed in claim 61, wherein the living plant is treated with a preparation as claimed in any one of claims 50 to 60. 30
65. A method of protecting a crop area against phytopathogenic fungi, wherein a crop area is treated with a compound selected from compounds of the general formula I given in claim 1, in which R and n have the meanings given in claim 1, and salts of such compounds of the general formula I. 30
66. A method as claimed in claim 65, wherein the crop area is treated with the compound claimed in any one of claims 5 to 24. 35
67. A method as claimed in claim 65, wherein the crop area is treated with the compound claimed in any one of claims 25 to 49. 35
68. A method as claimed in claim 65, wherein the crop area is treated with a preparation as claimed in any one of claims 50 to 60. 40
69. A method of protecting seeds against phytopathogenic fungi, wherein seeds are treated with a compound selected from compounds of the general formula I given in claim 1, in which R and n have the meanings given in claim 1, and salts of such compounds of the general formula I. 40
70. A method as claimed in claim 69, wherein the seeds are treated with the compound claimed in any one of claims 5 to 24. 45
71. A method as claimed in claim 69, wherein the seeds are treated with the compound claimed in any one of claims 25 to 49. 45
72. A method as claimed in claim 69, wherein the seeds are treated with a preparation as claimed in any one of claims 50 to 60. 50
73. A method as claimed in claim 69, conducted substantially as described in any one of Examples 4, 5, 8 and 9 herein. 50
74. A method as claimed in claim 69, conducted substantially as described in Example 6 or 7 herein. 50
75. A process for the manufacture of a compound of the general formula I

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in which R represents an aliphatic hydrocarbon group and n represents 1 or 2, or a salt thereof, wherein a compound of the general formula II



- 5 in which R has the meaning given above, is treated with an oxidizing agent, and, if desired, the resulting free compound is converted into a salt thereof by reaction with an inorganic or organic acid or a Lewis acid. 5
76. A process as claimed in claim 75, wherein R represents an aliphatic hydrocarbon group containing up to 5 carbon atoms.
- 10 77. A process as claimed in claim 76, wherein R represents an alkyl group containing 1 to 5 carbon atoms. 10
78. A process as claimed in any one of claims 75 to 77, wherein the oxidizing agent is an organic hydroperoxide, a per-acid, an N-halogeno-acid amide or an inorganic oxidizing agent.
- 15 79. A process for the manufacture of a compound of the general formula I given in claim 1, in which R and n have the meanings given in claim 1, or a salt thereof, conducted substantially as described in any one of Examples 1 to 3 herein. 15

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